

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
17 May 2001 (17.05.2001)

PCT

(10) International Publication Number  
WO 01/34658 A1

(51) International Patent Classification<sup>7</sup>: C08C 19/44,  
C08L 19/00, C08F 136/04

(21) International Application Number: PCT/US00/30743

(22) International Filing Date:  
10 November 2000 (10.11.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/165,172 12 November 1999 (12.11.1999) US

(71) Applicants (for all designated States except US):  
BRIDGESTONE CORPORATION [JP/JP]; 10-1,  
Kyobashi 1-chome, Chuo-ku, Tokyo 104 (JP). JSR COR-  
PORATION [JP/JP]; 11-24, Tsukiji 2-chome, Chuo-ku,  
Tokyo 104-8410 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): OZAWA, Yoichi  
[US/US]; 182 Hunt Club Drive, Apt. #2A, Copley, OH  
44321 (US). MILLER, H., Jerrold [US/US]; 471 St.

Leger Avenue, Akron, OH 44305 (US). MASAKI, Koji  
[JP/US]; 580 Park Hill Drive, Apt. 10, Fairlawn, OH 44333  
(US). FUJIMAKI, Tatsuo [JP/JP]; 3-2-3 Fujimi-cho, Hi-  
gashimurayama-shi, Tokyo (JP). SONE, Takuo [JP/JP];  
11-24 Tsukiji 2-chome, Chuo-ku, Tokyo 1104-8410 (JP).  
HATTORI, Iwakazu [JP/JP]; 11-24, Tsukiji 2-chome,  
Chuo-ku, Tokyo 104 (JP). MORITA, Koichi [JP/JP];  
3-972-56 Ko-han, Higashiyamato-shi, Tokyo (JP).

(74) Agents: BURLESON, David; Bridgestone/Firestone,  
Inc., 1200 Firestone Parkway, Akron, OH 44317 et al.  
(US).

(81) Designated States (national): CA, JP, US.

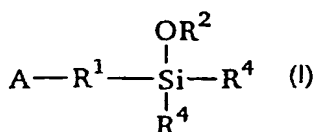
(84) Designated States (regional): European patent (AT, BE,  
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE, TR).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: MODIFIED POLYMERS PREPARED WITH LANTHANIDE-BASED CATALYSTS



(57) Abstract: A method for preparing a functionalized polymer comprising the steps of preparing a pseudo-living polymer by polymerizing conjugated diene monomer with a lanthanide-based catalyst, and reacting the pseudo-living polymer with at least one functionalizing agent defined by formula (I) where A is a substituent that will undergo an addition reaction with a pseudo-living polymer, R<sup>1</sup> is a divalent organic group, R<sup>2</sup> is a monovalent organic group, and each R<sup>4</sup>, which may be the same or different, is a monovalent organic group or a substituent defined by -OR<sup>5</sup> where R<sup>5</sup> is a monovalent organic group, with the proviso that A, R<sup>1</sup>, R<sup>2</sup>, R<sup>4</sup>, and R<sup>5</sup> are substituents that will not protonate a pseudo-living polymer. Also, the functionalized polymer and a vulcanizable composition containing the polymer.

WO 01/34658 A1

## MODIFIED POLYMERS PREPARED WITH LANTHANIDE-BASED CATALYSTS

This application gains priority from U.S. Patent Application Serial No. 60/165,172, filed November 12, 1999.

5

### FIELD OF THE INVENTION

This invention relates to functionalized polymers and processes for functionalizing these polymers. More particularly, the polymers are prepared with a lanthanide-based catalyst system and functionalized with certain functionalizing agents. Specifically, these functionalizing agents contain a alkoxysilane substituent that provides technologically useful benefits.

10

### BACKGROUND OF THE INVENTION

Conjugated diene polymers are commonly used in the rubber industry. These polymers are often prepared by using coordination-catalysis techniques because the microstructure of the resulting polymer can be controlled. Polybutadiene having greater than 90 percent of its units in the 1,4-*cis* configuration can be produced with a coordination catalyst system that includes a nickel, cobalt, or titanium compound, an alkylating agent, and a halogen source. Polymers having this microstructure have a low glass transition temperature ( $T_g$ ), which provides good low-temperature properties. Also, high 1,4-*cis* polymers have excellent wear resistance and mechanical properties such as reduced cut growth.

15

20

The tire industry has been challenged to design tires that have improved rolling resistance, which contributes to better fuel efficiency. Attempts to improve rolling resistance have included alternate tire designs and the use of rubber that has less hysteresis loss. Also, there has been a general trend toward the use of silica as a reinforcing filler. Polymers that interact with the fillers of tires have demonstrated less hysteresis loss.

25

Functionalized polymers prepared with anionic polymerization techniques have demonstrated lower hysteresis loss. They can be functionalized both at initiation and termination. Polybutadiene has been produced by initiating polymerization of 1,3-butadiene with functionalized initiators to provide polymers that have a greater affinity toward carbon black or silica fillers. Anionically

30

polymerized polymers have also been terminated with functionalized terminators to provide polymers that have a greater affinity toward silica fillers. Unfortunately because anionic polymerization does not provide strict control over the polymer microstructure, high 1,4-*cis* polymers are not obtained.

5            Coordination catalysis limits the ability to functionalize the resulting polymers because they operate by chemical mechanisms that involve the interaction of several chemical constituents, and often also involve self-termination reactions. As a result, the reaction conditions required to achieve functionalization are difficult to obtain.

Terminating agents, such as organo metal halides, heterocumulene compounds, three-membered heterocyclic compounds, and certain other halogen containing compounds, will react with polymers prepared with a Lanthanide-based catalyst system. The resulting functionalized polymers, however, do not have a useful enough affinity toward either silica or carbon black fillers. And, in general they do not alleviate the cold flow problems associated with neodymium produced polymers.

Therefore, there is a need in the art to provide functionalizing agents that will react with polymers prepared with coordination catalysts to yield functionalized polymers having a high *cis* microstructure and an affinity toward silica.

## SUMMARY OF INVENTION

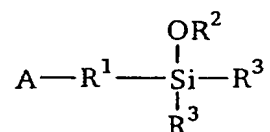
In general the present invention provides a method for preparing a functionalized polymer comprising the steps of preparing a pseudo-living polymer by polymerizing conjugated diene monomer with a lanthanide-based catalyst, and reacting the pseudo-living polymer with at least one functionalizing agent defined by the formula (I)



(I)

where A is a substituent that will undergo an addition reaction with a pseudo-living polymer, R<sup>1</sup> is a divalent organic group, each R<sup>2</sup>, which may be the same or different, is a monovalent organic group, and each R<sup>4</sup>, which may be the same or different, is a monovalent organic group or a substituent defined by -OR<sup>2</sup> and with the proviso that A, R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup>, are substituents that will not protonate a pseudo-living polymer.

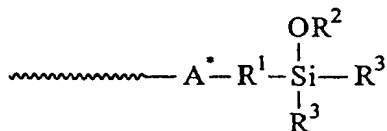
The present invention also includes a functionalized polymer prepared by a process comprising the steps of preparing a pseudo-living polymer by polymerizing conjugated monomer with a lanthanide-based catalyst, and reacting the pseudo-living polymer with a functionalizing agent defined by the formula (I)



(I)

where A is a substituent that will undergo an addition reaction with a pseudo-living polymer, R<sup>1</sup> is a divalent organic group, each R<sup>2</sup>, which may be the same or different, is a monovalent organic group, and each R<sup>4</sup>, which may be the same or different, is a monovalent organic group or a substituent defined by -OR<sup>2</sup> and with the proviso that A, R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup>, are substituents that will not protonate a pseudo-living polymer.

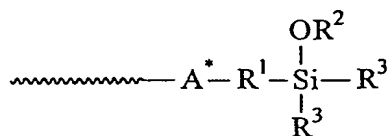
The present invention further provides a functionalized polymer defined by the formula (XI)



(XI)

where  $R^1$ ,  $R^2$ , and  $R^3$  are as defined above,  $A^*$  is the residue of a substituent that has undergone an addition reaction with a pseudo-living polymer, and  $\sim$  is polymer having a *cis* microstructure that is greater than about 85%, a 1,2- or 3,4-unit content that is less than about 3%, and a molecular weight distribution that is less than about 5.

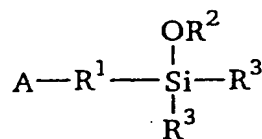
The present invention also provides a vulcanizable composition of matter comprising a rubber component comprising at least one functionalized polymer defined by the formula (XI)



(XI)

where  $R^1$ ,  $R^2$ , and  $R^3$  are as defined above,  $A^*$  is the residue of a substituent that has undergone an addition reaction with a pseudo-living polymer, and  $\sim$  is polymer having a *cis* microstructure that is greater than about 85%, a 1,2- or 3,4-unit content that is less than about 3%, and a molecular weight distribution that is less than about 5.

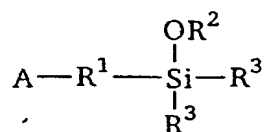
The present invention also provides a vulcanizable composition of matter comprising a rubber component comprising a functionalized polymer prepared by a process comprising the steps of preparing a pseudo-living polymer by polymerizing conjugated monomer with a lanthanide-based catalyst, and reacting the pseudo-living polymer with a functionalizing agent defined by the formula (I)



(I)

where A is a substituent that will undergo an addition reaction with a pseudo-living polymer,  $R^1$  is a divalent organic group, each  $R^2$ , which may be the same or different, is a monovalent organic group, and each  $R^4$ , which may be the same or different, is a monovalent organic group or a substituent defined by  $-OR^2$  and with the proviso that A,  $R^1$ ,  $R^2$ , and  $R^3$ , are substituents that will not protonate a pseudo-living polymer, and a reinforcing filler including an inorganic filler.

The present invention further provides a vulcanizable composition of matter comprising a rubber component comprising at least one functionalized polymer prepared by a process comprising the steps of preparing a pseudo-living polymer by polymerizing conjugated diene monomer with a lanthanide-based catalyst, and reacting the pseudo-living polymer with at least one functionalizing agent defined by the formula (I)



(I)

where A is a substituent that will undergo an addition reaction with a pseudo-living polymer,  $R^1$  is a divalent organic group, each  $R^2$ , which may be the same or different, is a monovalent organic group, and each  $R^4$ , which may be the same or different, is a monovalent organic group or a substituent defined by  $-OR^2$  and with the proviso that A,  $R^1$ ,  $R^2$ , and  $R^3$ , are substituents that will not protonate a pseudo-living polymer.

#### DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

The present invention is directed toward novel functionalizing agents, a process for functionalizing polymers prepared with lanthanide-based catalysts, the resulting functionalized polymers, and the use of these functionalized polymers within tires.

The polymers that are functionalized are prepared from lanthanide-based coordination catalyst systems. These polymers are preferably characterized

in that greater than about 85 percent of the polymer is in the *cis* microstructure, less than about 3% of the polymer is in the 1,2- or 3,4- microstructure, and molecular weight distribution of the polymer is less than about 4. Because these polymers have been found to demonstrate some living characteristics, they may be called pseudo-living polymers within this specification.

This invention is not limited to functionalizing a polymer prepared from any particular lanthanide-based catalyst. One useful catalyst includes a lanthanide compound, an alkylating agent, and a source of halogen. The lanthanide compound can include neodymium (Nd) carboxylates including Nd neodecanoate. Also, the lanthanide compound can include the reaction product of a Nd carboxylate and a Lewis base such as acetylacetone. The alkylating agents can generally be defined by the formula  $AlR_3$ , where each R, which may be the same or different, is hydrogen, a hydrocarbyl group, or an alkyl aluminoxy group, with the proviso that at least one R is a hydrocarbyl group. Examples of these alkylating agents include, but are not limited to, trialkyl aluminum, dialkyl aluminum hydride, alkyl aluminum dihydride, and mixtures thereof. Examples of alkylating agents where R is an alkyl aluminoxy group include methyl aluminoxanes. Sources of halogen can include organoaluminum chloride compounds. Catalyst systems that generally include lanthanide compounds and alkylating agents definable by the formula  $AlR_3$  are disclosed in U.S. Pat. Nos. 3,297,667, 3,541,063, and 3,794,604, which are incorporated herein by reference.

One particularly preferred catalyst includes (a) the reaction product of Nd carboxylate and acetylacetone, (b) triisobutylaluminum, diisobutylaluminum hydride, isobutylaluminum dihydride, or a mixture thereof, and (c) diethylaluminum chloride, ethylaluminum dichloride, or mixtures thereof. This catalyst system is disclosed in U.S. Pat. No. 4,461,883, which is incorporated herein by reference. Another preferred catalyst includes (a) Nd neodecanoate, (b) triisobutylaluminum, diisobutylaluminum hydride, isobutylaluminum dihydride, or a mixture thereof, and (c) diethylaluminum chloride, ethylaluminum dichloride, or mixtures thereof. This catalyst system is disclosed in Can. Pat. No. 1,223,396, which is incorporated herein by reference.

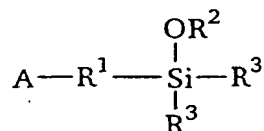
Still another preferred lanthanide-based catalyst system includes (a) a lanthanide compound such as Nd carboxylate, (b) an aluminoxane such as methyl aluminoxane, which may optionally be used in conjunction with an alkylating agent such as diisobutylaluminum hydride, and (c) a source of halogen such as diethylaluminum chloride. Neodymium catalysts that include alkyl aluminoxane compounds are described in Japanese Kokai publications 06-211916, 08-073515, 10-306113, and 11-035633, which are incorporated herein by reference. In an especially preferred embodiment of the system with aluminoxanes, the source of halogen is a metal halide of Group I, II, or VII metals. These metal halides include, but are not limited to, BeCl<sub>2</sub>, BeBr<sub>2</sub>, BeI<sub>2</sub>, MgCl<sub>2</sub>, MgBr<sub>2</sub>, MgI<sub>2</sub>, CaCl<sub>2</sub>, CaBr<sub>2</sub>, CaI<sub>2</sub>, BaCl<sub>2</sub>, BaBr<sub>2</sub>, BaI<sub>2</sub>, ZnCl<sub>2</sub>, ZnBr<sub>2</sub>, ZnI<sub>2</sub>, CdCl<sub>2</sub>, HgCl<sub>2</sub>, MnCl<sub>2</sub>, ReCl<sub>2</sub>, CuCl<sub>2</sub>, AgCl<sub>2</sub>, AuCl. Other lanthanide-based catalysts and processes for their use are described in U.S. Patent Nos. 4,444,903, 4,525,549, 4,699,960, 5,017,539, 5,428,119, 5,064,910, and 5,844,050, which are incorporated herein by reference.

Typically, from about 0.0001 to about 1.0 mmol of lanthanide metal are employed per 100 grams of monomer. More preferably, from about 0.001 to about 0.75, and even more preferably from about 0.005 to about 0.5 mmol of lanthanide metal per 100 grams of monomer are employed. The ratio of alkylating agent to lanthanide metal is from about 1:1 to about 1:500, more preferably from about 3:1 to about 250:1, and even more preferably from about 5:1 to about 200:1. The ratio of halogen source to lanthanide metal is from about 0.1:1 to about 30:1, more preferably from about 0.2:1 to about 15:1, and even more preferably from about 1:1 to about 10:1.

Monomers that are polymerized by the lanthanide-based catalysts are conjugated diene monomers that include, but are not limited to, 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, and myrcene. 1,3-butadiene is most preferred. These conjugated dienes may be used either alone or in combination. If desired, a small amount of monomer other than conjugated dienes can be added. These other monomers include, but are not limited to, aromatic vinyl compounds such as styrene. The amount of the copolymerizable monomer is not limited, but is usually less than 10 percent by weight (pbw) preferably less than 5 pbw, and even more preferably less than about 3 pbw of the entire polymer.



According to the present invention, pseudo-living polymers prepared with lanthanide-based catalysts are reacted with certain functionalizing agents to produce terminally-functionalized polymers. Functionalizing agents that can be used include those generally defined by the formula (I)



(I)

where A is a substituent that will undergo an addition reaction with a pseudo-living polymer,  $\text{R}^1$  is a divalent organic group, each  $\text{R}^2$ , which may be the same or different, is a monovalent organic group, and each  $\text{R}^3$ , which may be the same or different, is a monovalent organic group or a substituent defined by  $-\text{OR}^2$  and with the proviso that A,  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$ , are substituents that will not protonate a pseudo-living polymer. Preferably, at least one  $\text{R}^3$  is  $-\text{OR}^2$ , and even more preferably each  $\text{R}^3$  is  $-\text{OR}^2$ . As used throughout this specification, substituents that will not protonate a pseudo-living polymer refer to those substituents that will not donate a proton to the polymer in a protolysis reaction.

Preferably, the divalent organic groups are hydrocarbylene groups that contain from 0 to about 20 carbon atoms. More preferably, the hydrocarbylene groups will contain from about 1 to about 10 carbon atoms, and even more preferably from about 2 to about 8 carbon atoms. Those skilled in the art will appreciate that in the case where the hydrocarbylene group contains 0 carbon atoms, the group simply represents a single bond between the silicon atom and the group A. Suitable hydrocarbylene groups include, but are not limited to, alkylene, cycloalkylene, substituted alkylene, substituted cycloalkylene, alkenylene, cycloalkenylene, substituted alkenylene, substituted cycloalkenylene, arylene, and substituted arylene. The term "substituted" refers to an organic group, such as a hydrocarbyl group, that replaces a hydrogen atom attached to a carbon within the group. The hydrocarbylene groups may contain hetero atoms such as nitrogen (N), oxygen (O), sulfur (S), phosphorus (P), and silicon (Si). When these

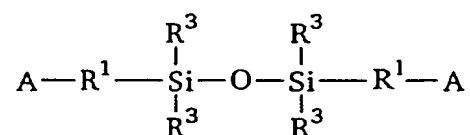
hydrocarbylene groups include O, they may be referred to as oxo-hydrocarbylene groups, or where they include N, they may be referred to as aza-hydrocarbyl-hydrocarbylene groups.

Some specific examples of hydrocarbylene groups include methylene,  
 5 ethylene, 1,3-propylene, 1,2-propylene, 1,4-butylene, 1,4-(2-methyl)butylene, 1,5-pentylene, cyclopentylene, and phenylene groups.

Preferably, the monovalent organic groups include hydrocarbyl groups that contain from 1 to about 20 carbon atoms. More preferably, these groups will include from about 2 to about 10 carbon atoms, and even more preferably from  
 10 about 3 to about 8 carbon atoms. These hydrocarbyl groups can include, but are not limited to, alkyl, cycloalkyl, substituted alkyl, substituted cycloalkyl, alkenyl, cycloalkenyl, substituted alkenyl, substituted cycloalkenyl, aryl, substituted aryl, allyl, aralkyl, alkaryl, and alkynyl, and may contain hetero atoms such as N, O, S, P, and Si. When these hydrocarbyl groups include O, they may be referred to as  
 15 oxo-hydrocarbyl groups, or where they include N, they may be referred to as aza-hydrocarbyl-hydrocarbyl groups.

Some specific examples of hydrocarbyl groups include methyl, ethyl, propyl, isopropyl, butyl, 2-methylbutyl, pentyl, hexyl, cyclohexyl, heptyl, octyl, cyclo-octyl, 2-ethylhexyl, and 2-propylhexyl groups.

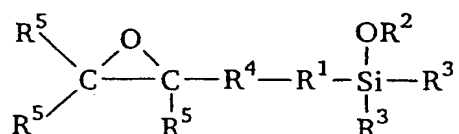
20 In addition to the monomeric alkoxysilane functionalizing agents that are generally represented by formula (I), dimers, trimers, or even larger oligomers of these compounds can be employed because these structures are likely to form in basic or acidic conditions or in the presence of condensation catalysts such as diorganotin dicarboxylate. For example, dimers of the compounds represented by  
 25 the formula (I) can be represented by the following formula



30 Reference to a monomeric alkoxysilane functionalizing agent will likewise refer to the oligomers thereof. In the event that R<sup>3</sup> is OR<sup>2</sup>, it may likewise couple with another functionalized polymer.

Substituents that will undergo an addition reaction with a pseudo-living polymer, and are therefore examples of substituent A, include epoxy groups, esters, imines including dihydroimidazoles, isocyanates, isothiocyanates, ketones, and imides including isocyanulate groups.

In one embodiment, where A contains an epoxy group, functionalizing agents of the present invention can be defined by the formula (II)



(11)

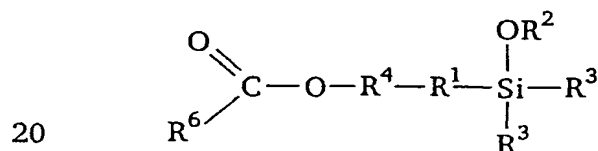
where R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are as defined above, R<sup>4</sup> is a divalent organic group or trivalent organic group where it forms a cyclic structure with R<sup>5</sup>, and each R<sup>5</sup>, which may be the same or different, is a hydrogen atom, a monovalent organic group, or a divalent organic group in the case where R<sup>4</sup> may form a cyclic structure with a R<sup>5</sup> group, or two R<sup>5</sup> groups may form a cyclic structure. R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> are substituents that will not protonate a pseudo-living polymer. The monovalent and divalent organic groups are as defined above.

Non-limiting examples of reactive epoxy groups include epoxy ethyl, epoxy propyl, methyl epoxy propyl, epoxy butyl, methyl epoxy butyl, epoxy pentyl, epoxy cyclohexyl, epoxy cycloheptyl, epoxy octyl, glycidoxypentyl, glycidoxybutyl, and glycidoxypentyl.

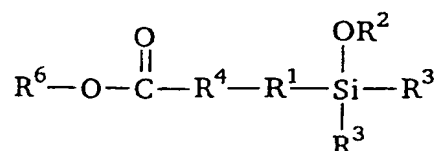
Specific non-limiting examples of epoxy-containing functionalizing agents definable by the formula (II) include 3-glycidoxypropyltrimethoxysilane (GPMOS), 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECMOS), 3-(trimethoxysilyl)propyl methacrylate, 3-glycidoxypropyl methyldiethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltriisopropoxysilane, 2-(3,4-epoxycyclohexyl)ethyltriphenoxysilane, (2-(3,4-epoxycyclohexyl)ethyl)methyldimethoxysilane, (2-(3,4-epoxycyclohexyl)ethyl)methyldiethoxysilane, (2-(3,4-

epoxycyclohexyl)ethyl)ethyldiethoxysilane, (2-(3,4-epoxycyclohexyl)ethyl)methyldiphenoxysilane, 3-glycidoxypropyltriethoxysilane, 3-glycidoxypropyltriisopropoxysilane, 3-glycidoxypropyltriphenoxysilane, (3-glycidoxypropyl)methyldimethoxysilane, (3-glycidoxypropyl)ethyldiethoxysilane, (3-glycidoxypropyl)methyldiphenoxysilane, partial condensation products of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, partial condensation products of 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane, partial condensation products of 2-(3,4-epoxycyclohexyl)ethyltriisopropoxysilane, partial condensation products of 2-(3,4-epoxycyclohexyl)ethyltriphenoxysilane, partial condensation products of 3-glycidoxypropyltrimethoxysilane, partial condensation products of 3-glycidoxypropyltriethoxysilane, partial condensation products of 3-glycidoxypropyltriisopropoxysilane, partial condensation products of 3-glycidoxypropyltriphenoxysilane.

In another embodiment, where A contains an ester group, functionalizing agents of the present invention can be defined by the formulas (III) and (IV)



(III)



(IV)

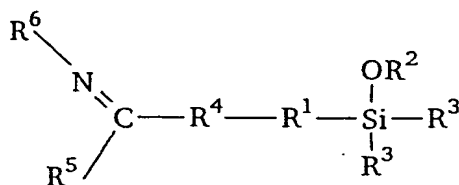
where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  are as defined above, and  $\text{R}^6$  is a monovalent organic group, or, in the case where  $\text{R}^4$  combines with  $\text{R}^6$  to form a cyclic group,  $\text{R}^6$  may be a divalent organic group and  $\text{R}^4$  will be a trivalent organic group, with the proviso that these substituents will not protonate a pseudo-living polymer. The monovalent and divalent organic groups are as defined above.

Non-limiting examples of ester groups include  $\alpha$ ,  $\beta$ -unsaturated esters, methacrylic acid esters, and acrylic acid esters.

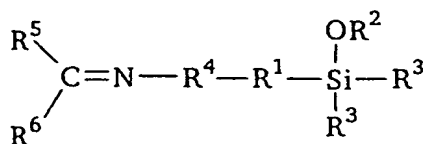
Specific non-limiting examples of ester-containing functionalizing agents definable by the formulas (III) and (IV) include 3-(trimethoxysilyl)propyl

methacrylate, 3-(meth)acryloyloxypropyltrimethoxysilane (MPMOS), 3-(meth)acryloyloxypropyltriethoxysilane, 3-(meth)acryloyloxypropyltriisopropoxysilane, 3-(meth)acryloyloxypropyltriphenoxysilane, (3-(meth)acryloyloxypropyl)methyldimethoxysilane, (3-(meth)acryloyloxypropyl)methyldiethoxysilane, (3-(meth)acryloyloxypropyl)ethyldiethoxysilane, (3-(meth)acryloyloxypropyl)methyldiphenoxysilane, partial condensation products of 3-(meth)acryloyloxypropyltrimethoxysilane, partial condensation products of 3-(meth)acryloyloxypropyltriethoxysilane, partial condensation products of 3-(meth)acryloyloxypropyltriisopropoxysilane, partial condensation products of 3-(meth)acryloyloxypropyltriphenoxysilane.

In another embodiment, where A contains an imine group, the functionalizing agent of the present invention can be defined by the formula (V) or formula (VI)



(V)



(VI)

at least one of R<sup>5</sup> or R<sup>6</sup> is attached to the imine carbon via a carbon atom, and R<sup>4</sup> is attached to the imine nitrogen via a carbon atom. R<sup>4</sup> may combine with R<sup>5</sup> or R<sup>6</sup> to form a cyclic group, or R<sup>5</sup> may combine with R<sup>6</sup> to form a cyclic group. All R groups are substituents that will not protonate a pseudo-living polymer. The mono- and divalent organic groups are as defined above.

Specific non-limiting examples of imine groups include alkylene amines, benzylideneamines, and imidazoles including 4,5-dihydroimidazoles.

Specific non-limiting examples of imine containing functionalizing agents definable by the formula (V) or (VI) include N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (TEOSI) and N-(1,3-dimethylbutylidene)-(3-triethoxysilyl)-1-propaneamine (HAPEOS).

In another embodiment, where A contains a ketone group, functionalizing agents of the present invention can be defined by the formula (VII)



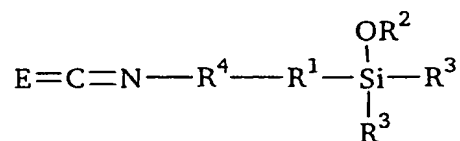
(VII)

25 where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> are as defined above, R<sup>4</sup> may combine with R<sup>5</sup> to form a cyclic group and where these substituents will not protonate a pseudo-living polymer. The monovalent and divalent organic groups are as defined above.

A non-limiting example of a ketone group includes benzophenone. Specific non-limiting examples of ketone-containing functionalizing agents definable by the formula (VII) include 4-(3-(triethoxysilyl)propoxy)benzophenone, 4-(3-(triethoxysilyl)ethyl)benzophenone, 4,4'-bis((3-

triethoxysilyl)propoxy)benzophenone, 4-(3-trimethoxysilyl)propoxybenzophenone, and 4,4'-bis((3-trimethoxysilyl)propoxy)benzophenone.

In another embodiment, where A contains an isocyanate or isothiocyanate group, functionalizing agents of the present invention can be defined by the formula (VIII)



10

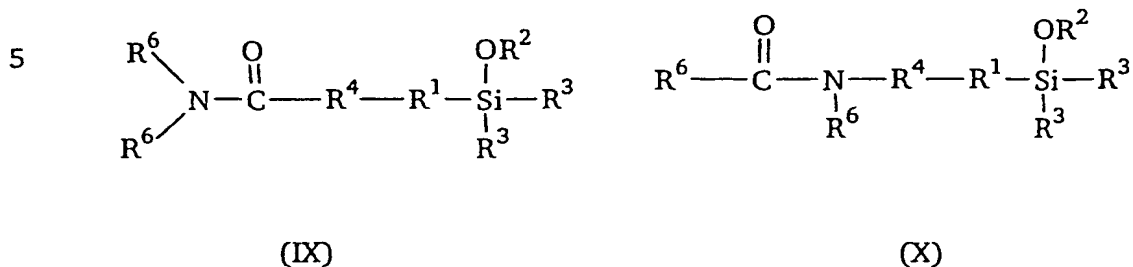
(VIII)

where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  are as defined above, and where E is O or S, with the proviso that these substituents will not protonate a pseudo-living polymer. The monovalent and divalent organic groups are as defined above.

Non-limiting examples of isocyanate groups include (2-isocyanato)ethyl, (3-isocyanato)propyl, (4-isocyanato)butyl, and (5-isocyanato)pentyl groups. The isothiocyanato equivalents of the foregoing groups are also suitable.

Specific non-limiting examples of isocyanate-containing functionalizing agents definable by the formula (VIII) include 3-isocyanatopropyltrimethoxysilane, 3-isocyanatopropyltriethoxysilane (IPMOS), 3-isocyanatopropyltriisopropoxysilane, 3-isocyanatopropyltriphenoxysilane, (3-isocyanatopropyl)methyldimethoxysilane, (3-isocyanatopropyl)methyldiethoxysilane, (3-isocyanatopropyl)methyldiphenoxysilane, partial condensation products of 3-isocyanatopropyltrimethoxysilane, partial condensation products of 3-isocyanatopropyltriethoxysilane, partial condensation products of 3-isocyanatopropyltriisopropoxysilane, partial condensation products of 3-isocyanatopropyltriphenoxysilane. Examples of isothiocyanate-containing functionalizing agents include the isothiocyanate equivalents of the foregoing isocyanate compounds.

In another embodiment, where A contains an amide group, functionalizing agents of the present invention can be defined by the formula (IX) or (X)



10

where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>6</sup> are as defined above. R<sup>4</sup> may combine with either R<sup>6</sup> to form a cyclic group, or two R<sup>6</sup> groups may combine to form a cyclic group. These substituents will not protonate a pseudo-living polymer. The monovalent and divalent organic groups are as defined above.

15

Non-limiting examples of amide groups include N-alkyl-isocyanulates, 3-(N,N-dialkylamido) propyl, trihydrocarbyl isocyanulate group, 3-(N,N-dihydrocarbylamido)alkyl group, N-hydrocarbylcaprolactam group, N-hydrocarbylpyrrolidone groups, and N,N-dialkylimidazolidione groups.

Specific non-limiting examples of amide-containing functionalizing agents definable by the formulas (IX) or (X) include tris(3-trimethoxysilylpropyl) isocyanulate, N-(3-trimethoxysilylpropyl)caprolactam, N-(3-trimethoxysilylpropyl)pyrrolidone, tris(3-triethoxysilylpropyl) isocyanulate (TMO5PI), -(3-triethoxysilylpropyl)caprolactam, and N-(3-triethoxysilylpropyl)pyrrolidone.

25

Epoxy compounds that will not protonate a pseudo-living polymer can be used in combination with the foregoing functionalizing agents to react with pseudo-living polymers to form blends of functionalized polymers. These epoxy compounds include, but are not limited to, styrene oxide, epoxidized soy bean oil, glycidyl (meth)acrylate, diglycidyl ether, ethylene oxide, propylene oxide, 1,2-epoxybutane, 1,2-epoxyisobutane, 2,3-epoxybutane, 1,2-epoxyhexane, 1,2-epoxyoctadecane, 1,2-epoxyeicosane, 1,2-epoxy-2-pentylpropane, 3,4-epoxy-1-butene, 1,2-epoxy-5-hexene, 1,2-epoxy-9-decene, 1,2-epoxycyclopentane, 1,2-

30



epoxycyclohexane, 1,2-epoxycyclododecane, 1,2-epoxyethylbenzene, 1,2-epoxy-1-methoxy-2-methylpropane, glycidyl methyl ether, glycidyl ethyl ether, glycidyl isopropyl ether, glycidyl phenyl ether, glycidyl butyl ether, ethyleneglycol diglycidyl ether, neopentylglycol diglycidyl ether, trimethylolpropane triglycidyl ether, glycerol triglycidyl ether, polypropyleneglycol diglycidyl ether, polyethyleneglycol diglycidyl ether, sorbitol polyglycidyl ether, N,N-diglycidylaniline, N,N-diglycidyltoluidine, N,N-diglycidyl-3-glycidoxyaniline, N,N-diglycidyl-2-glycidoxyaniline, bis(N,N-diglycidylamino)diphenylmethane, tris(2,3-epoxypropyl) isocyanurate, N,N-diglycidylbutylamine, and mixtures thereof.

Reference to any silane-containing functionalizing agents refers also to the condensation products of two or more kinds of silane-containing functionalizing agents.

Many of the functionalizing agents described herein are commercially available from chemical manufacturers such as Witco Chemical Corp., GE Silicone, Aldrich Chemical, Gelest, Inc., and Chisso Corp. of Japan. Alternatively, those skilled in the art can readily prepare these compounds by using conventional procedures. For example, the alkoxysilane compounds of this invention can be prepared by reacting an alcohol or a metal alkoxide with organosilicon halides. Organosilicon halides may be obtained reacting organometallic compounds, such as Grignard reagents or organolithium compounds, with silicon multi-halides ( $\text{SiCl}_4$ ,  $\text{MeSiCl}_3$ ), or by hydrosilation of olefinic compounds by halosilane compounds ( $\text{HSiCl}_3$  or  $\text{HMeSiCl}_2$ ).

The functionalized polymers of this invention are prepared by contacting one or more of the foregoing functionalizing agents, including mixtures thereof, with a pseudo-living polymer. If a solvent is employed, it is preferred to employ a solvent in which both the pseudo-living polymer and the functionalizing agent are soluble, or in which they may both be suspended. Preferably, this contacting takes place at a temperature of less than  $160^\circ\text{C}$ , and more preferably at a temperature from about  $20^\circ\text{C}$  to about  $130^\circ\text{C}$ . Further, the reaction time is preferably from about 0.1 to about 10 hours, and more preferably from about 0.2 to about 5 hours.

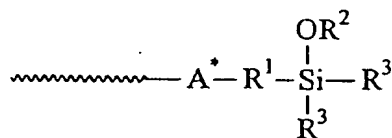
The amount of functionalizing agent used can vary. Preferably, from about 0.01 to about 200 moles of functionalizing agent per mole of lanthanide are employed, and more preferably, from about 0.1 to about 150 moles per mole of lanthanide.

5           The reaction between the pseudo-living polymer and the functionalizing agent is quenched by using reagents such as, but not limited to, isopropyl alcohol, methanol, and water. Stabilizers, such as 2,6-di-*tert*-butyl-4-methylphenol (BHT), can be added during or after quenching.

10           In lieu of or before quenching the resulting polymer, however, certain reactive compounds can be added to provide additional functionality to the polymer. These reactive compounds include those that will undergo addition reactions with metal alkoxides or metal amides. It is believed that metal alkoxides, or similar carbon-oxygen metal bonds, are produced when the compounds of formulas (II), (III), (IV), and (VII) are reacted with a pseudo-living polymer, where  
15           the metal is Al or Nd. Addition of a protic quenching agent is believed to remove the metal via a substitution reaction and thereby leave a hydroxyl group at the polymer chain end. A reaction between the metal alkoxide, or similar carbon-oxygen metal bonds, and the metal alkoxide-reactive compound before quenching is believed to provide additional functionality. For example, epoxy compounds will  
20           react with a metal alkoxide to form polyalkylene oxides. Some useful epoxy compounds include ethylene oxide and propylene oxide.

          The polymer product can be recovered by using any technique that is commonly employed in the art. For example, the polymer product can be coagulated in a hindered solvent such as isopropyl alcohol, and then dried in a hot  
25           air oven or hot mill. Alternatively, the polymer product can be recovered by steam desolventization and successive hot air drying or drying on a hot mill. A processing oil can be added prior to finishing.

          The resulting functionalized polymer can be represented by the formula  
(XI)



5

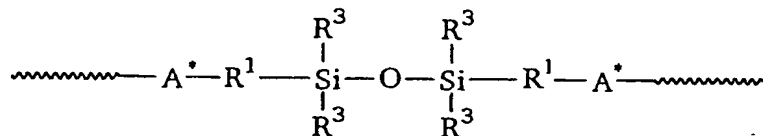
(XI)

where  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  are as defined above,  $\text{A}^*$  is the residue of a substituent that has undergone an addition reaction with a pseudo-living polymer, and   
 10 is polymer having a *cis* microstructure greater than about 85%, a vinyl content less than about 2%, and a molecular weight distribution that is less than about 5. More preferably, the polymer has a *cis* microstructure that is greater than about 90% a vinyl content that is less than about 1.5%, and a molecular weight distribution that is less than about 4.

15  $\text{A}^*$  is the reaction product of substituent A, a pseudo-living polymer, and optionally a quenching agent, as well as any additional reagents added prior to quenching. Where the substituent A of the functionalizing agent contains a reactive epoxy group, the reaction of this functionalizing agent and a pseudo-living polymer will undergo a ring-opening addition reaction, which leads to the  
 20 formation of a metal alkoxy group.

Polymers carrying alkoxy silane functionality may couple via a condensation reaction. For example, polymers represented by the formula (XI) may condense to form a coupled polymer that is represented by the following formula (XII)

25



(XII)

30 where  $\text{R}^1$  and  $\text{R}^3$  are as defined above.

Reference to the functionalized polymers will likewise include the condensation products thereof. In the event that any  $\text{R}^4$  is  $\text{OR}^5$ , it may likewise

couple with another functionalized polymer. Advantageously, the coupling of these functionalized polymers improves the cold flow resistance of the polymer.

The functionalized polymers of this invention can advantageously be used in the manufacture of various tire components including, but not limited to, tire treads, side walls, subreads, and bead fillers. They can be used as all or part of the elastomeric component of a tire stock. In one embodiment, the functionalized polymers comprise greater than about 10 pbw, more preferably, greater than about 20 pbw, and even more preferably greater than about 30 pbw, of the elastomeric component of a tire stock. Addition of the functionalized polymers to a tire stock does not alter the type or amount of other ingredients typically included within these vulcanizable compositions of matter. Accordingly, practice of this invention is not limited to any particular vulcanizable composition of matter or tire compounding stock.

Typically, tire stocks include an elastomeric component or rubber that is blended with reinforcing fillers and at least one vulcanizing agent. Accelerators, oils, waxes, fatty acids and processing aids are often included. Vulcanizable compositions of matter containing synthetic rubbers typically include antidegradants, processing oils, zinc oxide, optional tackifying resins, optional reinforcing resins, optional peptizers, and optional scorch inhibiting agents.

The functionalized polymers of this invention may be used in conjunction with other rubbers to form the elastomeric component of a tire stock. These other rubbers may include natural rubber, synthetic rubber, or both. Examples of synthetic rubber include synthetic poly(isoprene), poly(styrene-co-butadiene), poly(butadiene), poly(styrene-co-butadiene-co-isoprene) and mixtures thereof.

Reinforcing fillers may include both organic and inorganic fillers. Organic fillers include, but are not limited to carbon black, and inorganic fillers include, but are not limited to, silica, alumina, aluminum hydroxide, and magnesium hydroxide. Reinforcing fillers are typically employed in an amount from about 1 to about 100 parts by weight per 100 parts by weight rubber (phr), and preferably from about 20 to about 80 parts by weight phr, and more preferably from about 40 to about 80 parts by weight phr based on the total weight of all

reinforcing fillers employed. Typically, when an inorganic filler is used, it is used in combination with organic fillers. In these embodiments, the total amount of reinforcing filler will include from about 30 to about 99 parts by weight inorganic filler and 1 to about 70 parts by weight organic filler, based on 100 parts by weight total filler. More preferably, the total filler will include from about 50 to about 95 parts by weight inorganic filler and from about 5 to about 50 parts by weight organic filler based on 100 parts by weight filler.

Carbon blacks may include any commonly available carbon black, but those having a surface area (EMSA) of at least 20 m<sup>2</sup>/g, and more preferably at least 35 m<sup>2</sup>/g up to 200 m<sup>2</sup>/g or higher, are preferred. Surface area values used in this application are those determined by ASTM test D-1765 by using the cetyltrimethyl-ammonium bromide (CTAB) technique.

Silicas (silicon dioxide) are generally referred to as wet-process, hydrated silicas because they are produced by a chemical reaction in water, and precipitated as ultrafine, spherical particles. These particles strongly associate into aggregates that in turn combine less strongly into agglomerates. The surface area, as measured by the BET method, gives the best measure of the reinforcing character of different silicas. Useful silicas preferably have a surface area of about 32 to about 400 m<sup>2</sup>/g, preferably about 100 to about 250 m<sup>2</sup>/g, and more preferably about 150 to about 220 m<sup>2</sup>/g. The pH of the silica filler is generally about 5.5 to about 7 and preferably about 5.5 to about 6.8. Commercially available silicas include Hi-Sil<sup>TM</sup> 215, Hi-Sil<sup>TM</sup> 233, and Hi-Sil<sup>TM</sup> 190 (PPG Industries; Pittsburgh, Pennsylvania). Useful commercial grades of different silicas are also available from other sources including Rhone Poulenc.

Typically, a coupling agent is added when silica is used. One coupling agent conventionally used is bis-[3(triethoxysilyl) propyl]-tetrasulfide, which is commercially available under the tradename SI69 (Degussa, Inc.; New York, New York). Additional coupling agents may include bis(3-(triethoxysilyl)propyl) trisulfide, bis(3-(triethoxysilyl)propyl) disulfide, 3-mercaptopropyltriethoxysilane, bis(3-(trimethoxysilyl)propyl) tetrasulfide, bis(3-(trimethoxysilyl)propyl) trisulfide, bis(3-(trimethoxysilyl)propyl) disulfide, 3-mercaptopropyltrimethoxysilane, 3-(trimethoxysilyl)propyl)diethylthiocarbamyl tetrasulfide, and 3-

(trimethoxysilyl)propyl)benzothiazyl tetrasulfide. These agents are typically employed in an amount from about 1 to about 20 phr, and more preferably from about 3 to about 15 phr. Advantageously, less coupling agent is required when the functionalized polymers of this invention, which include a silane functionality, are employed.

Reinforced rubber compounds can be cured in a conventional manner with known vulcanizing agents. For example, sulfur or peroxide-based curing systems may be employed. For a general disclosure of suitable vulcanizing agents one can refer to Kirk-Othmer, *ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY*, 3<sup>rd</sup> Edition, Wiley Interscience, N.Y. 1982, Vol. 20, pp. 365-468, particularly *VULCANIZATION AGENTS AND AUXILIARY MATERIALS* pp. 390-402, or *Vulcanization* by A.Y. Coran, *ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING*, 2<sup>nd</sup> Edition, John Wiley & Sons, Inc., 1989. Vulcanizing agents may be used alone or in combination. This invention does not appreciably affect cure times. Typically, vulcanization is effected by heating the vulcanizable composition; e.g., it is heated to about 170°C. Cured or crosslinked polymers may be referred to as vulcanizates.

Tire formulations are compounded by using mixing equipment and procedures conventionally employed in the art. Preferably, an initial masterbatch is prepared that includes the elastomer component and the reinforcing fillers, as well as other optional additives such as processing oil and antioxidants. The polyolefin additives are preferably added during preparation of the initial masterbatch. Once this initial masterbatch is prepared, the vulcanizing agents are blended into the composition. The composition can then be processed into tire components according to ordinary tire manufacturing techniques including standard rubber curing techniques. Rubber compounding techniques and the additives employed therein are generally known as disclose in *The Compounding and Vulcanization of Rubber*, by Stevens in *RUBBER TECHNOLOGY SECOND EDITION* (1973 Van Nostrand Reinhold Company). Pneumatic tires can be made according to U.S. Patent Nos. 5,866,171; 5,876,527; 5,931,211; and 5,971,046, which are incorporated herein by reference.

The functionalized polymers of this invention can also be used in the manufacture of hoses, belts, shoe soles, window seals, other seals, vibration damping rubber, and other industrial products.

In order to demonstrate the practice of the present invention, the following examples have been prepared and tested as described in the Examples Section disclosed hereinbelow. The examples should not, however, be viewed as limiting the scope of the invention. The claims will serve to define the invention.

### EXAMPLES

#### 10    Examples 1-5

A catalyst was prepared by mixing 0.5 g of 1,3-butadiene monomer in hexanes, 0.32 mmol of Nd neodecanoate in hexanes, 31.7 mmol of methylaluminumoxane in toluene, and 6.67 mmol of diisobutylaluminum hydride in hexanes within a dried and N<sub>2</sub> purged bottle equipped with a rubber septum. After two minutes of contact, 1.27 mmol of diethylaluminum chloride in hexanes was added to the mixture. The mixture was then aged at room temperature for about 22 minutes.

Polybutadiene polymer was prepared by mixing the catalyst solution prepared above with 611 g of 1,3-butadiene monomer in about 3,460 g of hexanes at 24°C within a two-gallon stainless steel reactor equipped with an agitator and a jacket for temperature control. This mixture was agitated for about 11 minutes at 24°C. The jacket temperature was increased to 82°C and agitation continued for 33 minutes, after which the jacket temperature was lowered to 70°C. Approximately 370 g of the polymer cement was sampled into five dried and N<sub>2</sub> purged bottles, identified as examples 1-5 in Table I.

Examples 2-5 were then reacted with a functionalizing agent as set forth in Table I. A hexane solution or suspension of alkoxysilane functionalizing agent was added to the respective samples and allowed to react. The polymer was quenched with a small amount of isopropyl alcohol and 2,6-t-butyl 4-methyl phenol (BHT) in hexanes, and was isolated by coagulation in isopropyl alcohol and successive drum drying. Comparative Example 1 had a 93% *cis* structure and less

than 1% vinyl structure as determined by Fourier-Transform Infrared Spectroscopy (FTIR).

Table I also sets forth the Mooney Viscosity (ML 1+4 @ 100°C), the Mooney relaxation to 20% torque (T-80), the number average molecular weight ( $M_n$ ), the weight average molecular weight ( $M_w$ ), and molecular weight distribution as determined by GPC analysis, which was universally calibrated for polybutadienes based on polystyrene.

#### Examples 6-8

Polymers were prepared, functionalized, and analyzed as in Examples 1-5. Specifically, the catalyst solution was prepared by using 0.5 g of 1,3-butadiene in hexanes, 0.28 mmol of Nd neodecanoate in hexanes, 27.5 mmol of methylaluminoxane in toluene, 5.77 mmol of diisobutylaluminum hydride in hexanes, and 1.1 mmol of diethylaluminum chloride in hexanes. The catalyst solution was aged for 18 minutes, then mixed with additional 1,3-butadiene monomer at 27°C. The jacket temperature was increased to 82°C and the mixture was agitated for 42 minutes. Comparative Example 6 had 91% *cis* microstructure and less than 1% vinyl structure.

#### Examples 9 and 10

Polymers were prepared, functionalized, and analyzed as in Examples 1-5, except that the aging time between the addition of the diisobutylaluminum hydride and the diethylaluminum chloride was three minutes, and the aging time for the catalyst was 15 minutes. Polymerization was allowed to proceed for 60 minutes at 82°C, after which time the jacket temperature was lowered to 70°C. Comparative Example 9 had 93% *cis* microstructure and less than 1% vinyl structure.



TABLE I

	1	2	3	4	5	6	7	8	9	10
Alkoxysilane Functionalizing Agent	none	ECMOS	GPMOS	MPMOS	TMOSPI	none	TEOSI	TEOSI	none	HAPEOS
Amount of silane (eq /Nd)	—	20	20	20	20	—	25	25	—	50
Alkoxysilane Reaction Temp ("C)	—	50	50	50	50	—	50	50	—	50
Alkoxysilane Reaction Time (min)	—	30	30	30	30	—	180	900	—	180
ML1 + 4 @ 100 "C	28	62	103	63	62	44	74	84	40	59
T-80 (s)	3.3	6	14.2	5.7	5.7	4	5.3	5.3	3.7	4
Mn (kg/mol)	117	123	123	138	136	140	144	157	139	144
Mw (kg/mol)	241	284	245	319	600	274	294	305	273	289
Mw/Mn	2.1	2.3	2.0	2.3	4.4	2.0	2.0	1.9	2.0	2.0

Examples 11-15

A catalyst was prepared as in Examples 1-5, except that the catalyst was aged for 14 minutes at room temperature after charging the diethylaluminum chloride. Likewise, a similar polymerization technique was employed except that each example was functionalized with the same alkoxysilane functionalizing agent and then reacted for three hours, as set forth in Table II. Example 13 was desolventized by cast drying and successive vacuum oven drying. Examples 14 and 15 were treated with specified amounts of 2-ethylhexanoic acid (EHA), followed by 30 minutes of blending at 50°C. Example 14 was desolventized by isopropanol coagulation/drum drying, and Example 15 was desolventized by cast drying/vacuum oven drying. Comparative Example 11 had a 93% *cis* microstructure and less than 1% vinyl structure, and the yield was nearly stoichiometric.

TABLE II

	11	12	13	14	15
Alkoxysilane Functionalizing Agent	none	GPMOS	GPMOS	GPMOS	GPMOS
Amount of silane (eq/Nd)	—	50	50	50	50
Alkoxysilane Reaction Temp (°C)	—	50	50	50	50
Alkoxysilane Reaction Time (min)	—	180	180	180	180
Additive (eq/Nd)	none	none	none	EHA 20	EHA 20
ML1+4 @ 100°C	29	111	71	85	60
T-80 (s)	3.7	15.6	6.4	8.1	5.4
Mn (kg/mol)	121	135	121	135	125
Mw (kg/mol)	237	283	435	282	365
Mw/Mn	2.0	2.1	3.6	2.1	2.9

Examples 16-18

A catalyst solution containing 0.31 g of 1,3-butadiene, 0.57 mmol of Nd neodecanoate in hexanes, 56.7 mmol of methylaluminumoxane in toluene, 11.9 mmol of diisobutylaluminum hydride in hexanes, and 1.13 mmol of diethylaluminum chloride in hexanes was prepared as in Examples 1-5, and aged for 30 minutes at 50°C. 567 g of 1,3-butadiene in 3,213 g of hexanes was mixed with the catalyst at 24°C and agitated for 14 minutes. The jacket temperature was increased to 66°C and the mixture was agitated for another 52 minutes. The polymers obtained were sampled to three dried, N<sub>2</sub>-purged bottles, and labeled comparative examples 16, 17, and 18. Samples 17 and 18 were terminated with TEOS (tetra ethoxy silane). Comparative Example 16 had a 91% cis microstructure and less than 1% vinyl structure and the yield was nearly stoichiometric.

TABLE III

	16	17	18
Alkoxysilane Functionalizing Agent	none	TEOS	TEOS
Amount of silane (mmol)	—	3	7.5
Alkoxysilane Reaction temp (°C)	—	50	50
Alkoxysilane Reaction time (min)	—	30	30
ML1+4 @ 100°C	38	40	40
T-80 (s)	3.6	4.0	3.7
Mn (kg/mol)	113	106	109
Mw (kg/mol)	234	222	224
Mw/Mn	2.06	2.09	2.07

Examples 19-23

A catalyst solution was prepared within a dried and N<sub>2</sub> purged bottle by combining 2.7 g of 1,3-butadiene monomer in hexanes, 25.1 mmol of triisobutylaluminum in hexanes, and 2.14 mmol of diethylaluminum chloride in hexanes. After aging for 4.5 minutes at room temperature, 0.86 mmol of Nd neodecanoate in hexanes was added. The catalyst was aged for two minutes.

Polybutadiene polymer was prepared by mixing 611 g of 1,3-butadiene monomer and 3,460 g of hexanes with the catalyst solution prepared above at 27°C. After two minutes, the jacket temperature was increased to 82°C, and after an additional 68 minutes of agitation, the jacket temperature was lowered to 68°C.

5 This mixture was allowed to age for an additional 20 minutes, distributed to 5 separate bottles and labeled as Examples 19-23. Examples 21-23 were reacted with a alkoxysilane functionalizing agent as in Examples 1-5. The polymer was quenched and isolated as in Examples 1-5. Comparative Example 20 was reacted

10 with dioctyltin bis (2-ethyl hexyl maleate), a tin ester compound, in lieu of the alkoxysilane functionalizing agent. Comparative Example 19 had 97% *cis* microstructure and less than 1% vinyl structure.

TABLE IV

	19	20	21	22	23
Functionalizing or Coupling Agent	none	DOTBOM	GPMOS	GPMOS	GPMOS
Amount of Agent (eq/Nd)	—	1.2	0.3	1.2	5.0
Reaction Temp (°C)	—	50	50	50	50
Reaction Time (min)	—	60	900	900	900
ML1+4 @ 100°C	32.9	38.7	39.7	40.7	46.0
T-80 (s)	4.0	4.7	4.7	4.7	5.7
Mn (kg/mol)	111.8	111.1	110.1	113.7	111.6
Mw/Mn	2.76	2.81	2.97	2.90	3.06
Visual insoluble matter in THF at 0.02 w/v%	none	none	none	none	none
Cold flow resistance	1.96	—	—	2.27	—

Examples 24-36

A catalyst solution containing 0.024 grams of 1,3-butadiene, 0.09 mmol of Nd neodecanoate in cyclohexane, 7.2 mmol of methylaluminumoxane in toluene, 3.6 mmol of diisobutylaluminum hydride in toluene, and a source of halogen was prepared as in Examples 16-18, and aged for 30 minutes at about 50°C. The specific source of halogen used in each example as set forth in Table V, as well as the amount. The following abbreviations have been used: diethylaluminum chloride (DEAC), silicon tetrachloride (SiCl<sub>4</sub>), and zinc dichloride complexed with 1-decanol (ZnCl<sub>2</sub>). All of the halogen sources were employed as a toluene solution.

300 g of 1,3-butadiene in 2,400 g of cyclohexane was mixed with the catalyst at about 80°C for about one hour. The temperature was lowered to about 50°C and a functionalizing agent was added as set forth in Table V. The resulting polymers were quenched with a small amount of methanol solution and 2,6-*t*-butyl 4-methyl phenol (BHT) in hexanes. The polymer was isolated by steam desolventization and successive drum drying of the crumbs on a hot roll mill at about 110°C.

In Examples 29-32, prior to quenching, 4.5 mmol of a secondary terminator was added and allowed to react for about 30 minutes at 50°C. The terminator used included styrene oxide (Sty-O) and epoxydized soy bean oil (E-SBO). The amount of E-SBO was based on the number of epoxy groups on the molecule.

The resulting polymers were each individually compounded into a rubber formulation that employed silica (Nipsil VN3™; Nippon Silica; Japan). Namely, an initial masterbatch was blended within an internal mixer at an initial temperature of about 110°C for about 3.5 minutes. The masterbatch was allowed to cool and then re-milled within the same internal mixer for about 2 minutes. Then, a cure system was added while the compound was continually processed within the internal mixer at a temperature of about 80°C for about 1 minute. The compounding recipe that was employed is set forth in the following table.

## COMPOUNDING RECIPE

	Ingredient	Parts per Hundred Rubber
	Elastomer	100
	Aromatic Oil	10
5	Silica	50
	Stearic Acid	2
	Antioxidant	1
	Masterbatch Total	163
10	Zinc Oxide	2.5
	Sulfur	1.3
	Accelerators	2.8
	Total	169.6

15           Once compounded, each formulation was press cured at about 160°C. The cured samples were then analyzed to determine tensile strength at break and elongation at break according to JIS-K6301. Also, the samples were tested to determine  $\tan \delta$  at 50°C (frequency at 100 rad/s and 3 percent strain), as well as Lambourne wear (Shimada Giken, Co. Ltd., Japan; at a load of 4.5 kg, a slip ratio of 60 percent, and a temperature of 50°C). The results of this testing are provided in Table V. The values of  $\tan \delta$  and Lambourne wear were normalized against Example 41, and are therefore indexes, with higher values indicating better results.

20



TABLE V

	24	25	26	27	28
Source of Halogen	DEAC	SiCl <sub>4</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>
Amount of Halogen Source (mmol)	0.18	0.05	0.09	0.09	0.09
Functionalizing Agent	GPMOS	GPMOS	GPMOS	IPMOS	MPMOS
Amount of functionalizing agent (mmol)	4.50	4.50	4.50	4.50	4.50
Functionalizing Agent Reaction Time (min)	30	30	30	30	30
Functionalizing Agent Reaction Temp (°C)	50	50	50	50	50
1,4-cis microstructure (%)	96.3	96.4	97.6	97.5	97.4
1,2 microstructure (%)	1.3	1.3	0.9	1.0	0.9
ML1+4 @ 100 °C	39	40	43	44	42
Mw/Mn	3.1	3.1	2.5	2.5	2.5
Tensile Strength at Break (MPa)	15.7	15.9	16.8	16.7	16.7
Elongation at Break (%)	580	575	580	585	580
Tan δ at 50 °C (index)	133	134	142	143	142
Lambourne Wear (index)	124	126	135	134	134

5

10

15

20

25

TABLE V (CONTINUED)

	29	30	31	32	33	34	35
Source of Halogen	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	DEAC	SiCl <sub>4</sub>	ZnCl <sub>2</sub>	none
Amount of Halogen Source (mmol)	0.09	0.09	0.09	0.18	0.05	0.09	0.00
Functionalizing Agent	GPMOS	GPMOS	GPMOS	—	—	—	GPMOS
Amount of functionalizing agent (mmol)	4.50	4.50	4.50	—	—	—	4.50
Functionalizing Agent Reaction Time (min)	10	10	10	—	—	—	30
Functionalizing Agent Reaction Temp (°C)	50	50	50	—	—	—	50
Secondary Terminator	Sly-O	E-SBO	MPMOS	—	—	—	—
1,4-cis microstructure (%)	97.5	97.5	97.6	96.3	96.4	97.6	82.4
1,2 microstructure (%)	0.9	0.9	1.0	1.3	1.3	0.9	2.4
ML1+4 @ 100 °C	36	41	43	29	28	28	45
Mw/Mn	2.8	2.8	2.8	2.7	2.5	2.1	4.8
Tensile Strength at Break	17.1	17.4	18.0	14.8	14.7	14.5	11.7
Elongation at Break (%)	570	575	580	590	580	580	400
Tan δ at 50 °C	142	143	150	118	119	121	65
Lambourne Wear	136	137	142	110	112	116	77

Examples 36-41

5 A catalyst solution containing 0.1 grams of 1,3-butadiene, 0.37 mmol of Nd neodecanoate, 11.1 mmol of triisobutylaluminum in toluene, 3.7 mmol of diisobutylaluminum hydride, and 0.74 mmol of diethylaluminum chloride was prepared as in Examples 24-36. 300 grams of 1,3-butadiene monomer were polymerized in 2,400 g of cyclohexane, and the resulting polymer was terminated as set forth in Table VI. The resulting polymers were compounded as in Examples 24-36. Comparative Example 41, which was a commercially obtained high-*cis* polybutadiene polymer (BR01™; Japan Synthetic Rubber, Tokyo, Japan), was  
10 tested according to the procedures employed in Examples 24-35, including compounding.

TABLE VI

	36	37	38	39	40	41
Source of Halogen	DEAC	DEAC	DEAC	DEAC	None	—
Amount of Halogen Source (mmol)	0.74	0.74	0.74	0.74	None	—
Functionalizing Agent	GPMOS	IPMOS	MPMOS	—	—	—
Amount of functionalizing agent (mmol)	4.50	4.50	4.50	—	—	—
Functionalizing Agent Reaction Time (min)	50	50	50	—	—	—
Functionalizing Agent Reaction Temp (°C)	30	30	30	—	—	—
1,4-cis microstructure (%)	96.6	96.5	96.6	96.5	3.1	95.0
1,2 microstructure (%)	1.2	1.2	1.2	1.2	6.3	2.5
ML1+4 @ 100 °C	36	37	40	33	n/a	45
Mw/Mn	2.9	2.9	2.9	2.3	6.2	4.0
Tensile Strength at Break (MPa)	16.5	16.4	16.5	14.6	n/a	13.2
Elongation at Break (%)	585	575	580	575	n/a	550
Tan δ at 50 °C (index)	139	139	140	115	n/a	100
Lambourne Wear (index)	133	134	133	111	n/a	100

Examples 42-51

Examples 26, 34, and 41 were each compounded into a formulation that included a second elastomer as part of the elastomeric component of the rubber formulation. The formulations were compounded as in Examples 24-41, and the  
5 cured stocks were similarly analyzed.

Table VII sets forth the specific polymers employed in each example, as well as the amounts thereof. NR is natural rubber, and SBR is styrene-butadiene copolymer, which was experimentally synthesized using *n*-butyllithium. The SBR contained 35 percent by weight styrene, and 21% vinyl in the butadiene units, and  
10 was terminated with tin tetrachloride. The Lambourne wear and tan  $\delta$  values in Table VII were normalized against Example 48.

TABLE VII

Examples	42	43	44	45	46	47	48	49	50	51
Polymer Example Number	26	26	26	34	34	34	41	26	34	41
Amount of Polymer (phr)	50	10	5	50	10	5	50	50	50	50
Other Elastomer	NR	NR	NR	NR	NR	NR	NR	SBR	SBR	SBR
Amount of Other Elastomer (phr)	50	90	95	50	90	95	50	50	50	50
Modulus at 300% (MPa)	13.8	14.4	15.7	13.1	14.2	15.6	12.6	12.9	11.7	11.3
Tensile at Break (MPa)	26.3	26.5	27.3	23.1	25.3	27.2	22.5	24.1	21.5	20.5
Elongation at Break (%)	450	480	500	470	480	500	460	390	400	400
Lambourne Wear	130	111	96	104	94	78	100	123	97	94
Tan $\delta$ at 50 °C	125	110	95	105	93	91	100	121	97	91

Examples 53-60

Examples 26 and 35 were compounded into a tire formulation that included natural rubber as a second elastomeric component and contained varying amounts of silica filler. The compounding recipe and test methods were the same as in Examples 42-51, except that the amount of silica used in each example was varied as set forth in Table VIII, and bis(3(triethoxysilyl) propyl) tetrasulfide (SI69™; Degussa-Hüls, Germany) was used as a silane coupling agent in Examples 57 and 59. The Lambourne wear and tan  $\delta$  were normalized against Example 58.

TABLE VIII

Examples	52	53	54	55	56	57	58	59
Polymer Example Number	26	26	26	26	26	26	34	34
Amount of Polymer (phr)	50	50	50	50	50	50	50	50
Other Elastomer	NR	NR	NR	NR	NR	NR	NR	NR
Amount of Other Elastomer (phr)	50	50	50	50	50	50	50	50
Silica (phr)	100	50	30	130	10	50	50	50
Silane Coupling Agent (phr)	—	—	—	—	—	5	—	5
Modulus at 300% (MPa)	15.1	14.0	12.8	9.4	10.1	15.5	13.1	13.6
Tensile at Break (MPa)	27.5	28.5	23.5	17.1	18.2	29.1	23.1	25.5
Elongation at Break (%)	420	450	460	210	510	410	470	430
Lambourne Wear	135	130	114	77	84	141	100	118
Tan $\delta$ at 50°C	129	127	117	81	83	139	100	118

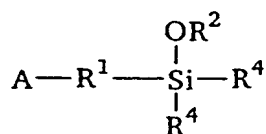


Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth herein.

## CLAIMS

What is claimed is:

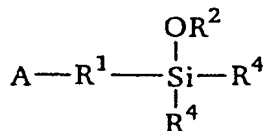
- 1 1. A method for preparing a functionalized polymer comprising the steps of:  
2 preparing a pseudo-living polymer by polymerizing conjugated diene  
3 monomer with a lanthanide-based catalyst; and  
4 reacting the pseudo-living polymer with at least one functionalizing  
5 agent defined by the formula (I)



(I)

12 where A is a substituent that will undergo an addition reaction with a pseudo-  
13 living polymer,  $\text{R}^1$  is a divalent organic group,  $\text{R}^2$  is a monovalent organic  
14 group, and each  $\text{R}^4$ , which may be the same or different, is a monovalent  
15 organic group or a substituent defined by  $-\text{OR}^5$  where  $\text{R}^5$  is a monovalent  
16 organic group, with the proviso that A,  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^4$ , and  $\text{R}^5$  are substituents  
17 that will not protonate a pseudo-living polymer.

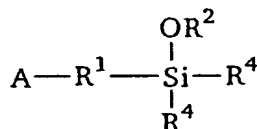
- 1 2. A functionalized polymer prepared by a process comprising the steps of:  
2 preparing a pseudo-living polymer by polymerizing conjugated monomer  
3 with a lanthanide-based catalyst; and  
4 reacting the pseudo-living polymer with a functionalizing agent defined  
5 by the formula (I)



(I)

where A is a substituent that will undergo an addition reaction with a pseudo-living polymer,  $R^1$  is a divalent organic group,  $R^2$  is a monovalent organic group, and each  $R^4$ , which may be the same or different, is a monovalent organic group or a substituent defined by  $-OR^5$  where  $R^5$  is a monovalent organic group, with the proviso that A,  $R^1$ ,  $R^2$ ,  $R^4$ , and  $R^5$  are substituents that will not protonate a pseudo-living polymer.

3. A vulcanizable composition of matter comprising:
  - a rubber component comprising a functionalized polymer prepared by a process comprising the steps of
    - preparing a pseudo-living polymer by polymerizing conjugated monomer with a lanthanide-based catalyst; and
    - reacting the pseudo-living polymer with a functionalizing agent defined by the formula (I)

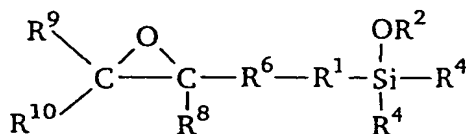


(I)

where A is a substituent that will undergo an addition reaction with a pseudo-living polymer,  $R^1$  is a divalent organic group,  $R^2$  is a monovalent organic group, and each  $R^4$ , which may be the same or different, is a monovalent organic group or a substituent defined by  $-OR^5$  where  $R^5$  is a monovalent organic group, with the proviso that A,  $R^1$ ,  $R^2$ ,  $R^4$ , and  $R^5$  are substituents that will not protonate a pseudo-living polymer, where said polymer has a cis microstructure that is greater than about 90 percent, a 1,2- or 3,4- unit content that is less than about 2 percent, and a molecular weight distribution that is less than about 4; and

a reinforcing filler including an inorganic filler.

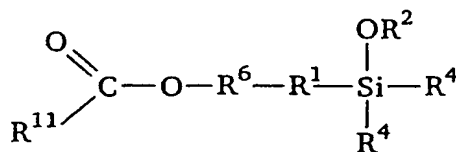
4. The method of claim 1, polymer of claim 2, or vulcanizable composition of claim 3, where the functionalizing agent is defined by the formula (II)



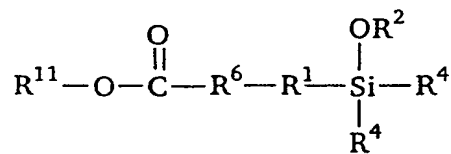
(II)

where  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^4$  are as defined above,  $\text{R}^6$  is a divalent organic group, and  $\text{R}^8$  and  $\text{R}^9$ , which may be the same or different, are hydrogen atoms or monovalent organic groups, or, in the case where  $\text{R}^6$  combines with  $\text{R}^8$ ,  $\text{R}^9$ , or  $\text{R}^{10}$  to form a cyclic group, or  $\text{R}^8$  combines with  $\text{R}^9$  or  $\text{R}^{10}$  to form a cyclic group,  $\text{R}^6$  may be a trivalent organic group and  $\text{R}^8$ ,  $\text{R}^9$ , and  $\text{R}^{10}$  may be divalent organic groups, with the proviso that these substituents will not protonate a pseudo-living polymer.

5. The method of claim 1, polymer of claim 2, or vulcanizable composition of claim 3, where the functionalizing agent is defined by the formulas (III) & (IV)



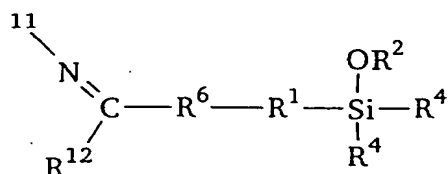
(III)



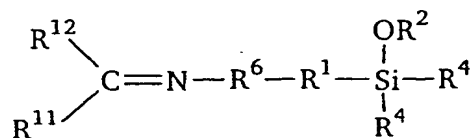
(IV)

where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^6$  are as defined above, and  $\text{R}^{11}$  is a monovalent organic group, or, in the case where  $\text{R}^6$  combines with  $\text{R}^{11}$  to form a cyclic group,  $\text{R}^6$  may be a trivalent organic group and  $\text{R}^{11}$  may be a divalent organic group, with the proviso that these substituents will not protonate a pseudo-living polymer.

6. The method of claim 1, polymer of claim 2, or vulcanizable composition of claim 3, where the functionalizing agent is defined by the formulas (V) or (VI)



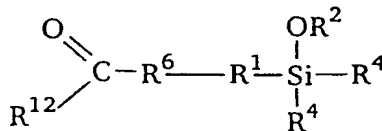
(V)



(VI)

where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^4$ ,  $\text{R}^6$ , and  $\text{R}^{11}$  are as defined above, and  $\text{R}^{12}$  is a hydrogen atom or a monovalent organic group, with the proviso that at least one of  $\text{R}^{12}$  or  $\text{R}^6$  in formula (V) is attached to the imine carbon via a carbon atom,  $\text{R}^{11}$  or  $\text{R}^{12}$  in formula (VI) is attached to the imine carbon via a carbon atom,  $\text{R}^{11}$  in formula (V) is attached to the imine nitrogen via a carbon atom, and  $\text{R}^6$  in formula (VI) is attached to the imine nitrogen via a carbon atom, or, in the case where  $\text{R}^6$  combines with  $\text{R}^{11}$  or  $\text{R}^{12}$  to form a cyclic group, or  $\text{R}^{11}$  combines with  $\text{R}^{12}$  to form a cyclic group,  $\text{R}^6$  may be a trivalent organic group, and  $\text{R}^{11}$  and  $\text{R}^{12}$  may be divalent organic groups, with the proviso that these substituents will not protonate a pseudo-living polymer.

7. The method of claim 1, polymer of claim 2, or vulcanizable composition of claim 3, where the functionalizing agent is defined by the formula (VII)

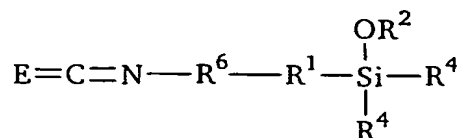


(VII)

where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^4$ ,  $\text{R}^6$ , and  $\text{R}^{12}$  are as defined above, or, in the case where  $\text{R}^6$  combines with  $\text{R}^{12}$  to form a cyclic group,  $\text{R}^6$  may be a trivalent organic group and

12 R<sup>12</sup> may be a divalent organic group, with the proviso that these substituents will  
13 not protonate a pseudo-living polymer.

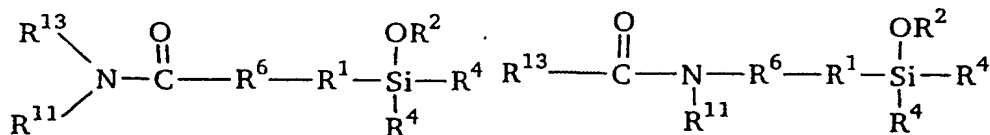
1 8. The method of claim 1, polymer of claim 2, or vulcanizable composition of  
2 claim 3, where the functionalizing agent is defined by the formula (VIII)



(VIII)

10 where R<sup>1</sup>, R<sup>2</sup>, R<sup>4</sup>, and R<sup>6</sup> are as defined above, and where E is an oxygen atom  
11 or a sulfur atom, with the proviso that these substituents will not protonate a  
12 pseudo-living polymer.

1 9. The method of claim 1, polymer of claim 2, or vulcanizable composition of  
2 claim 3, where the functionalizing agent is defined by the formulas (IX) or (X)



(IX)

(X)

10 where R<sup>1</sup>, R<sup>2</sup>, R<sup>4</sup>, R<sup>6</sup>, and R<sup>11</sup> are as defined above, and R<sup>13</sup> is a monovalent  
11 organic group, or, in the case where R<sup>6</sup> combines with R<sup>11</sup> or R<sup>13</sup> to form a cyclic  
12 group, or R<sup>11</sup> and R<sup>13</sup> combine to form a cyclic group, R<sup>6</sup> may be a trivalent  
13 organic group and R<sup>11</sup> and R<sup>13</sup> may be divalent organic groups, with the proviso  
14 that these substituents will not protonate a pseudo-living polymer.

- 1 10. The method of claim 1, polymer of claim 2, or vulcanizable composition of
- 2 claim 3, further comprising the step of quenching the polymer.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 00/30743

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08C19/44 C08L19/00 C08F136/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08C C08L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 767 179 A (BRIDGESTONE CORP) 9 April 1997 (1997-04-09)	2-10
Y	abstract page 4, line 46 -page 5, line 20 page 6, line 36 - line 39 examples 1,2 table 1 claims 1-10	1,4-10
Y	EP 0 894 825 A (NIPPON ZEON CO) 3 February 1999 (1999-02-03) abstract page 6, line 10 - line 25 page 8, line 42 - line 54 page 9, line 27 - line 57 tables 1,2 claims 9-20	1,4-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

1 February 2001

Date of mailing of the international search report

26/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl  
Fax: (+31-70) 340-3016

Authorized officer

Denis, C



# INTERNATIONAL SEARCH REPORT

In ternational Application No  
PCT/US 00/30743

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>EP 0 863 165 A (JSR CORP)            9 September 1998 (1998-09-09)            abstract            page 4, line 55 -page 5, line 16            page 9, line 4 - line 17            page 9, line 29 - line 44            page 10, line 2 - line 45            examples 4,6,11            table 4            claims 1-19</p> <p>-----</p>	1,4-10

# INTERNATIONAL SEARCH REPORT

Information on patent family members

In tional Application No

PCT/US 00/30743

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0767179 A	09-04-1997	JP 9087426 A US 6117927 A	31-03-1997 12-09-2000
EP 0894825 A	03-02-1999	WO 9739056 A	23-10-1997
EP 0863165 A	09-09-1998	JP 11035633 A JP 10306113 A	09-02-1999 17-11-1998